Supporting information
For
DABCO Catalyzed Synthesis of 3-Substituted-3-Hydroxyindolin-2-ones in
Aqueous Media

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Contents

- General remarks
- General experimental procedure
- Characterization data for compounds
- Copies of ^1H and ^{13}C NMR

General remarks

Commercially available isatins and acetophenones from Aldrich and urea from Spectrochem. were used. Progress of reactions was monitored by thin layer chromatography (TLC). NMR spectra were recorded in Acetone d_6 at 300 MHz for ^1H and 75 MHz for ^{13}C on Bruker Avance DPX-300MHz . Chemical shifts were reported in δ (ppm) relative to Acetone d_6 (^{13}C) as internal standards. Integrals are in accordance with assignments, coupling constants are given in Hz. The HRMS was recorded on a JOEL-AccuTOF JMS-T100LC Mass spectrometer having a DART source. Yields refer to quantities obtained after chromatography.

General experimental procedure

A solution of 0.5 gm (3.4 mmol) of isatin (**1**), 0.408 gm (3.4 mmol) of acetophenone (**2**) and 0.080 gm (0.72 mmol) of DABCO in water (15 mL) was heated to 80 °C for 1-3 hours. After the completion of reaction which was indicated by TLC, the solid which separated out was collected and washed with water. In some cases, the reaction mixture was extracted with ethyl acetate as the solid was not getting filtered off and combined organic layer was evaporated to give solid reaction mixture. Although, the TLC indicated the completion of both starting material, the reaction mixture was purified by column chromatography on silica gel by using 40% of EA: hexane mixture to provide light yellow product in good to excellent yields.

Characterisation data for selected compounds

3-hydroxy-3-(2-oxo-2-phenylethyl)indolin-2-one (3a) m.p. 165-167 °C; 90% as light yellow solid; ¹H NMR (Acetone d₆, 300 MHz) δ = 9.41 (bs, 1H, NH), 7.95 (d, *J* = 9 Hz, 2H, Ar-H), 7.61 (t, *J* = 6 Hz, 1H, Ar-H), 7.48 (t, *J* = 6 Hz, 2H, Ar-H), 7.35 (d, *J* = 6 Hz, 1H, Ar-H), 7.19 (t, *J* = 9 Hz, 1H, Ar-H), 6.93-6.98 (m, 2H, Ar-H), 5.18 (bs, 1H, OH), 4.11 (d, *J* = 18 Hz, 1H, CH), 3.72 (d, *J* = 18 Hz, 1H, CH) ¹³C NMR (Acetone d₆, 75 MHz) 197.3, 178.9, 143.9, 137.6, 134.1, 132.4, 130.1, 129.5 (2C), 128.9 (2C), 124.6, 122.4, 110.5, 75.5, 46.4 HRMS (ESI) *m/z* for C₁₆H₁₃NO₃ [M + H]⁺, calcd, 268.0973, found, 268.0979

3-(2-(4-bromophenyl)-2-oxoethyl)-3-hydroxyindoline-2-one (3b) m.p. 170-172 °C; 81% as light yellow solid; ¹H NMR (Acetone d₆, 300 MHz) δ = 9.34 (bs, 1H, NH), 7.91 (t, *J* = 6 Hz, 1H, Ar-H), 7.88 (t, *J* = 6 Hz, 1H, Ar-H), 7.70 (t, *J* = 3 Hz, 1H, Ar-H), 7.67 (t, *J* = 3 Hz, 1H, Ar-H), 7.35-7.32 (m, 1H, Ar-H), 7.22-7.17 (m, 1H, Ar-H), 6.92-6.89 (m, 1H, Ar-H), 5.11 (bs, 1H, OH), 4.07 (d, *J* = 18 Hz, 1H, CH), 3.67 (d, *J* = 18 Hz, 1H, CH) ¹³C NMR (Acetone d₆, 75 MHz) 197.1, 179.2, 144.4, 137.2, 133.2, 132.8, 131.4, 130.7, 129.1, 125.2 (2C), 122.9 (2C), 111.0, 75.0, 46.9 HRMS (ESI) *m/z* for C₁₆H₁₂BrNO₃ [M + H]⁺, calcd, 346.0078, found, 346.0084

3-hydroxy-3-(2-oxo-2-(*p*-tolyl)ethyl)indolin-2-one (3d) m.p. 140-142 °C; 85% as light yellow solid; ¹H NMR (Acetone d₆, 300 MHz) δ = 9.32 (bs, 1H, NH), 7.85 (d, *J* = 9 Hz, 2H, Ar-H), 7.34-7.28 (m, 3H, Ar-H), 7.19 (dt, *J* = 12 Hz, 1H, Ar-H), 6.91-6.87 (m, 2H, Ar-H), 5.10 (bs, 1H, OH), 4.04 (d, *J* = 18 Hz, 1H, CH), 3.66 (d, *J* = 18 Hz, 1H, CH) 2.38 (s, 3H, Ar-

CH₃) ¹³C NMR (Acetone d₆, 75 MHz) 197.5, 179.3, 145.4, 144.5, 135.8, 133.0, 130.6, 129.5 (2C), 125.1 (2C), 122.9, 111.0, 75.1, 46.8, 22.1 HRMS (ESI) *m/z* for C₁₇H₁₅NO₃ [M + H]⁺, calcd, 282.1130, found, 282.1134

3-hydroxy-3-(2-(4-methoxyphenyl)-2-oxoethyl)indolin-2-one (3e) m.p. 174-176 °C; 79% as light yellow solid; ¹H NMR (Acetone d₆, 300 MHz) δ = 9.33 (bs, 1H, NH), 7.94 (d, *J* = 9 Hz, 2H, Ar-H), 7.32 (d, *J* = 9 Hz, 1H, Ar-H), 7.18 (t, *J* = 6 Hz, 1H, Ar-H), 6.99 (d, *J* = 9 Hz, 2H, Ar-H), 6.89 (t, *J* = 6 Hz, 2H, Ar-H), 5.15 (bs, 1H, OH), 4.01 (d, *J* = 18 Hz, 1H, CH) 3.87 (s, 1H, OMe) 3.63 (d, *J* = 18 Hz, 1H, CH) ¹³C NMR (Acetone d₆, 75 MHz) 195.9, 178.9, 164.7, 143.9, 132.6, 131.2, 130.7, 130.0 (2C), 124.6 (2C), 122.3, 114.6, 110.5, 74.6, 56.0, 45.9 HRMS (ESI) *m/z* for C₁₇H₁₅NO₄ [M + H]⁺, calcd, 298.1079, found, 298.1072

3-hydroxy-3-(2-(4-nitrophenyl)-2-oxoethyl)indolin-2-one (3f) m.p. 170-172 °C; 90% as light yellow solid; ¹H NMR (Acetone d₆, 300 MHz) δ = 9.42 (bs, 1H, NH), 8.34 (t, *J* = 3 Hz, 1H, Ar-H), 8.31 (t, *J* = 3 Hz, 1H, Ar-H), 8.21 (t, *J* = 3 Hz, 1H, Ar-H), 8.18 (t, *J* = 3 Hz, 1H, Ar-H), 7.36 (d, *J* = 6 Hz, 1H, Ar-H), 7.21 (dt, *J* = 6 Hz, 1H, Ar-H), 6.94-6.91 (m, 2H, Ar-H) 5.19 (bs, 1H, OH) 4.18 (d, *J* = 18 Hz, 1H, CH) 3.78 (d, *J* = 18 Hz, 1H, CH) ¹³C NMR (Acetone d₆, 75 MHz) 196.8, 178.9, 151.6, 144.1, 142.4, 132.3, 130.6, 130.5, 129.9 (2C), 125.1, 124.8 (2C), 122.8, 110.9, 74.7, 47.3 HRMS (ESI) *m/z* for C₁₆H₁₂N₂O₅ [M + H]⁺, calcd, 313.0824, found, 313.0852

5-bromo-3-hydroxy-3-(2-oxo-2-phenylethyl)indolin-2-one (3g) m.p. 177-179 °C; 75% as light yellow solid; ¹H NMR (Acetone d₆, 300 MHz) δ 9.48 (bs, 1H, NH), 7.96 (d, *J* = 6 Hz, 2H, Ar-H), 7.62 (t, *J* = 6 Hz, 1H, Ar-H), 7.55-7.48 (m, 3H, Ar-H), 7.37 (dd, *J* = 3 Hz, 6 Hz, 1H, Ar-H), 6.90 (d, *J* = 9 Hz, 1H, Ar-H), 5.27 (bs, 1H, OH), 4.19 (d, *J* = 18 Hz, 1H, CH) 3.78 (d, *J* = 18 Hz, 1H, CH) ¹³C NMR (Acetone d₆, 75 MHz) 197.7, 178.8, 143.9, 138.0, 135.5, 134.8, 133.3, 130.1 (2C), 129.4, 128.4 (2C), 114.8, 112.8, 75.0, 47.1 HRMS (ESI) *m/z* for C₁₆H₁₂BrNO₃ [M + H]⁺, calcd, 346.0078, found, 346.0107

5-bromo-3-(2-(4-bromophenyl)-2-oxoethyl)-3-hydroxyindolin-2-one (3h) m.p. 180-183 °C; 78% as light yellow solid; ¹H NMR (Acetone d₆, 300 MHz) δ 9.51 (bs, 1H, NH), 7.90 (d, *J* = 3 Hz, 2H, Ar-H), 7.70 (d, *J* = 9 Hz, 2H, Ar-H), 7.53 (s, 1H, Ar-H), 7.37 (dd, *J* = 6 Hz, 3 Hz, 1H, Ar-H), 6.90 (d, *J* = 9 Hz, 1H, Ar-H), 5.31 (bs, 1H, OH), 4.17 (d, *J* = 18 Hz, 1H, CH) 3.76 (d, *J* = 18 Hz, 1H, CH) ¹³C NMR (Acetone d₆, 75 MHz) 196.4, 178.3, 143.2, 136.4, 134.8,

132.8, 132.7, 130.8 (2C), 128.7 (2C), 127.9, 114.4, 112.3, 74.3, 46.53 HRMS (ESI) m/z for $C_{16}H_{11}Br_2NO_3$ $[M + H]^+$, calcd, 423.9183, found, 423.9185

5-bromo-3-hydroxy-3-(2-(4-methoxyphenyl)-2-oxoethyl)indolin-2-one (3i) mp. 170-172 °C; 86% as white crystalline solid; 1H NMR (Acetone d_6 , 300 MHz) δ 9.45 (bs, 1H, NH), 7.93 (d, J = 9 Hz, 1H, Ar-H), 7.52 (s, 1H, Ar-H), 7.36 (dd, J = 9 Hz, 3 Hz, 1H, Ar-H), 7.01 (d, J = 9 Hz, 2H, Ar-H), 6.88 (d, J = 9 Hz, 1H, Ar-H), 5.26 (bs, 1H, OH), 4.09 (d, J = 18 Hz, 1H, CH) 3.88 (s, 3H, OMe) 3.70 (d, J = 18 Hz, 1H, CH) ^{13}C NMR (Acetone d_6 , 75 MHz) 195.96, 178.7, 165.1, 143.6, 135.4, 133.0, 131.54 (2C), 130.7 (2C), 128.1, 114.9, 114.5, 112.5, 74.8, 56.3, 46.4 HRMS (ESI) m/z for $C_{17}H_{14}BrNO_4$ $[M + H]^+$, calcd, 376.0184, found, 376.0177

5-bromo-3-hydroxy-3-(2-oxo-2-(p-tolyl)ethyl)indolin-2-one (3j) m.p. 154-156 °C; 75% as light yellow solid; 1H NMR (Acetone d_6 , 300 MHz) δ 9.47 (bs, 1H, NH), 7.85 (d, J = 6 Hz, 2H, Ar-H), 7.53 (s, 1H, Ar-H), 7.35-7.29 (m, 3H, Ar-H), 6.88 (d, J = 9 Hz, 1H, Ar-H), 5.26 (bs, 1H, OH), 4.13 (d, J = 18 Hz, 1H, CH), 3.73 (d, J = 18 Hz, 1H), 2.38 (s, 3H, Ar-CH₃) ^{13}C NMR (Acetone d_6 , 75 MHz) 197.3, 178.9, 145.6, 143.9, 135.6, 133.2, 130.6 (2C), 129.5 (2C), 128.4 (2C), 114.8, 112.8, 75.0, 46.9, 22.1, HRMS (ESI) m/z for $C_{17}H_{14}BrNO_3$ $[M + H]^+$, calcd, 360.0235, found, 360.0230

5-chloro-3-hydroxy-3-(2-oxo-2-phenylethyl)indolin-2-one (3l) m.p. 140-142 °C; 87% as light yellow solid; 1H NMR (Acetone d_6 , 300 MHz) δ 9.47 (bs, 1H, NH), 7.96 (d, J = 6 Hz, 2H, Ar-H), 7.62 (t, J = 6 Hz, 1H, Ar-H), 7.50 (t, J = 6 Hz, 2H, Ar-H), 7.42 (d, J = 3 Hz, 1H, Ar-H), 7.23 (dd, J = 6 Hz, 1H, Ar-H), 6.93 (d, J = 9 Hz, 1H, Ar-H), 5.27 (bs, 1H, OH) 4.17 (d, J = 18 Hz, 1H, CH) 3.78 (d, J = 18 Hz, 1H, CH) ^{13}C NMR (Acetone d_6 , 75 MHz) 197.2, 178.5, 142.9, 137.5, 134.6, 134.2, 129.8, 129.5 (2C), 128.9 (2C), 127.1, 125.1, 111.8, 74.5, 46.5 HRMS (ESI) m/z for $C_{16}H_{12}ClNO_3$ $[M + H]^+$, calcd, 302.0583, found, 302.0584

3-(2-(4-bromophenyl)-2-oxoethyl)-5-chloro-3-hydroxyindolin-2-one (3m) m.p. 165-167 °C; 80% as light yellow solid; 1H NMR (Acetone d_6 , 300 MHz) δ 9.51 (bs, 1H, NH), 7.90 (t, J = 3 Hz, 1H, Ar-H), 7.88 (t, J = 3 Hz, 1H, Ar-H), 7.70 (t, J = 3 Hz, 1H, Ar-H), 7.67 (t, J = 3 Hz, 1H, Ar-H), 7.41 (d, J = 3 Hz, 1H, Ar-H), 7.23 (dd, J = 6 Hz, 3 Hz, 1H, Ar-H), 6.94 (d, J = 9 Hz, 1H, Ar-H) 5.31 (bs, 1H, OH) 4.17 (d, J = 18 Hz, 1H, CH), 3.76 (d, J = 18 Hz, 1H, CH) ^{13}C NMR (Acetone d_6 , 75 MHz) 196.7, 178.6, 143.0, 136.6, 134.6, 133.0, 131.1 (2C), 130.2, 129.0 (2C), 127.4, 125.4, 112.1, 74.7, 46.8, HRMS (ESI) m/z for $C_{16}H_{11}BrClNO_3$ $[M + H]^+$, calcd, 379.9689, found, 379.9693

5-chloro-3-hydroxy-3-(2-(4-methoxyphenyl)-2-oxoethyl)indolin-2-one (3n) m.p. 160-162 °C; 84% as light yellow solid; ¹H NMR (Acetone d₆, 300 MHz) δ 9.46 (bs, 1H, NH), 7.95-7.92 (m, 2H, Ar-H), 7.40 (d, *J* = 3 Hz, 1H, Ar-H), 7.22 (dd, *J* = 6 Hz, 3 Hz, 1H, Ar-H), 7.01-6.98 (m, 2H, Ar-H), 6.92 (d, *J* = 9 Hz, 1H, Ar-H), 5.27 (bs, 1H, OH), 4.09 (d, *J* = 18 Hz, 1H, CH) 3.87 (s, 3H, OMe) 3.70 (d, *J* = 18 Hz, 1H, CH) ¹³C NMR (Acetone d₆, 75 MHz) 196.2, 179.1, 165.3, 143.4, 135.2, 131.7, 131.0, 130.3 (2C), 127.5 (2C), 125.6, 115.1, 112.3, 75.2, 56.5, 46.6 HRMS (ESI) *m/z* for C₁₇H₁₄ClNO₄ [M + H]⁺, calcd, 332.0689, found, 332.0695

5-chloro-3-hydroxy-3-(2-oxo-2-(*p*-tolyl)ethyl)indolin-2-one (3o) m.p. 145-147 °C; 88% as light yellow solid; ¹H NMR (Acetone d₆, 300 MHz) δ 9.48 (bs, 1H, NH), 7.86-7.84 (m, 2H, Ar-H), 7.41 (d, *J* = 3 Hz, 1H, Ar-H), 7.31-7.28 (m, 2H, Ar-H), 7.22 (dd, *J* = 6 Hz, 3 Hz, 1H, Ar-H), 6.93 (d, *J* = 6 Hz, 1H, Ar-H), 5.27 (bs, 1H, OH), 4.13 (d, *J* = 18 Hz, 1H, CH) 3.74 (d, *J* = 18 Hz, 1H, CH) ¹³C NMR (Acetone d₆, 75 MHz) 197.0, 178.8, 145.3, 143.1, 135.3, 134.9, 130.4, 130.1, 129.3 (2C), 127.3 (2C), 125.3, 112.0, 74.8, 46.7, 21.8 HRMS (ESI) *m/z* for C₁₇H₁₄ClNO₃ [M + H]⁺, calcd, 316.0740, found, 316.0748

Copies of ¹H and ¹³C NMR

Fig. 1: ¹H spectraof 3-hydroxy-3-(2-oxo-2-phenylethyl)indolin-2-one (**3a**)

Fig. 2: ¹³C spectra of 3-hydroxy-3-(2-oxo-2-phenylethyl)indolin-2-one (**3a**)

Fig. 3: ¹H spectra of 3-hydroxy-3-(2-oxo-2-(p-tolyl)ethyl)indolin-2-one (**3d**)

Fig. 4: ^{13}C spectra of 3-hydroxy-3-(2-oxo-2-(p-tolyl)ethyl)indolin-2-one (**3d**)

Fig. 5: ^1H spectra of 3-hydroxy-3-(2-(4-methoxyphenyl)-2-oxoethyl)indolin-2-one (**3e**)

Fig. 6: ^{13}C spectra of 3-hydroxy-3-(2-(4-methoxyphenyl)-2-oxoethyl)indolin-2-one (**3e**)

Fig. 7: ¹H spectra of 5-bromo-3-hydroxy-3-(2-oxo-2-phenylethyl)indolin-2-one (**3g**)

Fig. 8: ^{13}C spectra of 5-bromo-3-hydroxy-3-(2-oxo-2-phenylethyl)indolin-2-one (**3g**)

Fig. 9: ¹H spectra of 5-bromo-3-(2-(4-bromophenyl)-2-oxoethyl)-3-hydroxyindolin-2-one (**3h**)

Fig. 10: ¹³C spectra of 5-bromo-3-(2-(4-bromophenyl)-2-oxoethyl)-3-hydroxyindolin-2-one (**3h**)

Fig. 11: 1H spectra of 5-bromo-3-hydroxy-3-(2-(4-methoxyphenyl)-2-oxoethyl)indolin-2-one (**3i**)

Fig. 12: ^{13}C spectra of 5-bromo-3-hydroxy-3-(2-(4-methoxyphenyl)-2-oxoethyl)indolin-2-one (**3i**)

Fig. 13: ¹H spectra of 5-chloro-3-hydroxy-3-(2-oxo-2-phenylethyl)indolin-2-one (**31**)

Fig. 14: ^{13}C spectra of 5-chloro-3-hydroxy-3-(2-oxo-2-phenylethyl)indolin-2-one (**3l**)

Fig. 15: ¹H spectra of 3-(2-(4-bromophenyl)-2-oxoethyl)-5-chloro-3-hydroxyindolin-2-one (**3m**)

Fig. 16: ^{13}C spectra of 3-(2-(4-bromophenyl)-2-oxoethyl)-5-chloro-3-hydroxyindolin-2-one (**3m**)

Fig. 17: ¹H spectra of 5-chloro-3-hydroxy-3-(2-(4-methoxyphenyl)-2-oxoethyl)indolin-2-one (**3n**)

Fig. 18: ^{13}C spectra of 5-chloro-3-hydroxy-3-(2-(4-methoxyphenyl)-2-oxoethyl)indolin-2-one (**3n**)

Fig. 19: ¹H spectra of 5-chloro-3-hydroxy-3-(2-oxo-2-(p-tolyl)ethyl)indolin-2-one (**3o**)

Fig. 20: ^{13}C spectra of 5-chloro-3-hydroxy-3-(2-oxo-2-(p-tolyl)ethyl)indolin-2-one (**3o**)